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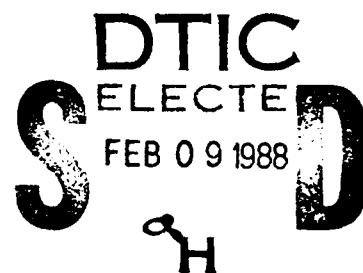
PHYSICAL AND MECHANICAL PROPERTIES OF AMERICAN CYANAMID'S  
ACETYLENE-TERMINATED PREPREG SYSTEM: T-300/CATB-44

D.B. Curliss  
Structural Materials Branch  
Nonmetallic Materials Division

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AIR FORCE WRIGHT AERONAUTICAL LABORATORIES  
AIR FORCE SYSTEMS COMMAND  
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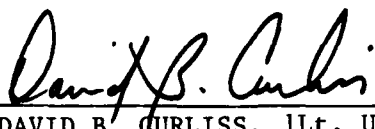
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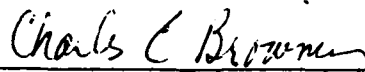
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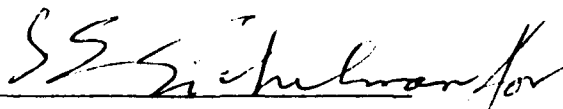


DAVID B. GURLISS, 1Lt, USAF  
Structural Materials Branch  
Nonmetallic Materials Division



CHARLES E. BROWNING, Chief  
Structural Materials Branch  
Nonmetallic Materials Division

FOR THE COMMANDER



MERRILL L. MINGES, Director  
Nonmetallic Materials Division

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) A carbon-fiber-reinforced modified Acetylene-Terminated (AT) resin carbon-fiber composite, designated T-300/CATB-44, was evaluated for its potential as a 400°F to 450°F structural material with a good balance of properties. Such a composite is needed for advanced Air Force aircraft and weapons systems. AT resins have demonstrated good high-temperature capability, but lack the "toughness" of State-of-the-Art Bismaleimide (BMI) resins. Under AF contract F33615-84-C-5050, American Cyanamid attempted to improve the toughness of an AT resin without compromising its high-temperature performance capability; their product is designated CATB-44. Composite test panels were fabricated from prepreg provided by American Cyanamid. These panels were machined into test specimens for the "standard" AFWAL/MLBC material characterization. Thermophysical characteristics of the prepreg were measured. Physical and Mechanical properties of the cured composite were also determined. The results from these tests are compared to the first-generation T-300/V378A carbon-fiber-reinforced bismaleimide composite. The RT mechanical properties of the T-300/CATB-44 were generally comparable to the T-300/V378A composite. The elevated dry and wet properties of T-300/CATB-44 generally showed 50 to 70 percent retention of RT dry properties and were marginally superior in most cases to the T-300/V378A elevated temperature performance.					
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## SECTION 1. INTRODUCTION

The evaluation of new organic matrix composite materials to assess their potential for use on current and future Air Force weapons systems is part of an ongoing in-house research task at the AFWAL Materials Laboratory. The purpose of the task is to provide chemical and mechanical property data for proposed organic matrix composite materials. The test matrix used in this evaluation is given in Table 1. The test matrix is not intended to generate a comprehensive design database, but rather to provide a critical comparison between material systems with the minimum amount of material and time investment. We have devised this testing plan to enable us to screen materials for various military aerospace system applications.

Table 1. Mechanical Tests and Conditions.

TEST ID	LAYUP	TEST CONDITIONS **
3-Pt Flexure	[0] <sub>12</sub>	RT d,w 350°F d,w
4-Pt Flexure	[0] <sub>12</sub>	RT d,w 350°F d,w
4-Pt Flexure	[90] <sub>12</sub>	RT d,w
Short Beam Shear (SBS)	[0] <sub>12</sub>	RT d,w 350°F d,w
4-Pt Shear	[0] <sub>12</sub>	RT d,w 350°F d,w
0° Tension	[0] <sub>12</sub>	RT d
In-Plane-Shear (IPS)	[±45] <sub>2S</sub>	RT d, 350°F d
Edge Delamination (ED)	[±30,+30,90] <sub>2S</sub>	RT d
Double Cantilever Beam (DCB)	[0] <sub>24</sub>	RT d
End Notched Flexure (ENF)	[0] <sub>24</sub>	RT d

\*\* "d" indicates vacuum dried and desiccant storage; "w" indicates water soak at 70°C to saturation and testing in this state

This report is a summary of the physical and mechanical properties of one candidate high-temperature thermosetting composite system. The American Cyanamid resin CATB-44 prepregged on Thornel T-300 carbon fibers was evaluated using the AFWAL/MLBC material characterization program for its potential as an advanced structural composite material. In addition, because the CATB-44 resin

exhibited some unusual morphological characteristics, physical evaluation beyond the scope of the standard evaluation was carried out.

Section 2 gives the background of the development and motivation for the development of the toughened AT resin system. The discussion describes some of the basic requirements for the resin system and how the CATB-44 system was developed to meet those needs. Section 3 is a description of the experimental methods employed during this research. The procedures used to characterize the T-300/CATB-44 prepreg, fabricate the composite test specimens, and test the composite specimens are described. Section 4 gives a discussion of the results of the various tests in Section 3. Also, in Section 4 we compare and contrast these results with another competitive aerospace composite material. Finally, in Section 5 we give some brief conclusions and recommendations for further efforts with the T-300/CATB-44 system.

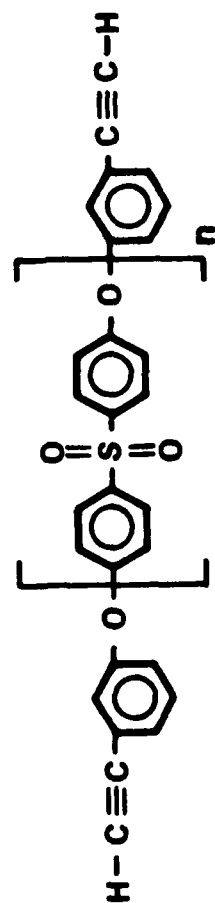
## SECTION 2. BACKGROUND

One of the major problems with current aerospace resins is the degradation of performance at their maximum service temperature in a humid environment--the so called "hot/wet" performance. State-of-the-art epoxy matrix composites generally have a maximum service temperature of approximately 250°F, while the latest toughened BMI systems are in the 350°F range. Both of these materials systems are processable with comparable techniques and equipment and are toughened sufficiently for structural applications while maintaining the required mechanical properties at elevated temperatures. A new class of thermosetting resins have been developed that have potential for application in the 450°F range. These materials are the Acetylene Terminated (AT) resins. Because they are addition curing thermosets they are processable via routes that are similar to those currently being employed to process epoxies and BMIs. An advantage the ATs have over epoxies and BMIs is that they cure without any amine compound. Thus, they have very low relative moisture absorption compared to the other aerospace thermosetting resins.

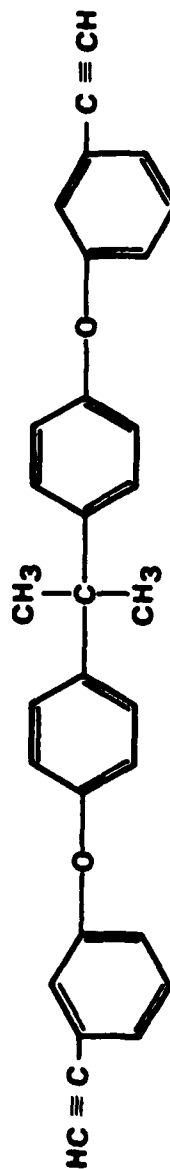
Recently a great deal of work has been done with AT resins for high-temperature composite matrix applications (Lee et al., 1983), and Hergenrother (1984) has written an excellent overview of the synthesis of different acetylene-terminated pre-polymers and of their physical properties. Dynes (1985) evaluated several unformulated AT resins. He investigated HR600P, ATB (isopropylidiphenol), m-ATS (sulphonyldiphenol), and ATP (BATQ-H). He found that they could be easily prepregged onto an unsized AS4 fiber using a hot-melt prepregger, and that they could be processed into good quality void-free laminates. The AT resins did have very good moisture resistance. The neat resins typically absorbed less than 0.5% water as compared to 2% or more with epoxies and BMIs. The resins did not exhibit the plasticization effect with water absorption that epoxies and BMIs do. However, the AT/carbon fiber composites exhibited poor interfacial bonding, brittle failure modes,

and micro-cracking in quasi-isotropic laminates. Furthermore, even though the property retention was good at elevated temperatures (350°F) the flexural properties were less than those of state-of-the-art epoxies. American Cyanamid (1987) attempted to optimize the AT resins ATB and m-ATS for use as high temperature composite matrix materials. The molecular structures of the ATB and ATS prepolymers are shown in Figure 1.

The dry Tg (measured using TMA) of the ATB and ATS networks were determined to be 282°C and 338°C respectively. However, American Cyanamid found that the Tg of ATS dropped significantly more than the ATB when attempts were made to toughen it. For this reason, and also so that more work could be done optimizing the ATB, the ATS was dropped from the scope of work under the contract. The initial objective in their optimization was to exceed RT mechanical performance and toughness of first generation BMI matrices (like V378A), have 350°F wet service capability and handle/process similarly to contemporary epoxies and BMIs. The secondary objective was to maintain 450°F wet service capability with improved RT toughness. Some of the generic toughening techniques that have been successful with epoxies and BMIs were applied to the AT systems. In this case, the approach was to introduce a tougher second phase into the brittle ATB resin. The second phase was introduced in a variety of fractions to cause it to range from being located in isolated domains to being the continuous phase with the ATB as the discrete domains. These various resin formulations were tried and screened using different criteria at different levels of the process. The final level of resin screening requirements were quite stringent. Some of the more important requirements were a dry Tg between 400 and 500°F, retention of 80% RT dry properties at 450°F wet conditions, and a RT dry flexural failure strain of 5%.



(a)



(b)

Figure 1. Acetylene Terminated "monomers." "a" is m-ATS and "b" is ATB.

## SECTION 3. EXPERIMENTAL METHODS

### 3.1 Overview

The experimental portion of this investigation was divided into the following three phases: a) Prepreg/Resin Characterization; b) Composite Panel Fabrication; and c) Composite Mechanical Properties Evaluation.

### 3.2 Prepreg/Resin Characterization

The Prepreg/Resin Characterization was a basic assessment of the physical properties of the prepreg and of the flow characteristics and chemical kinetics of the resin system. This information gave us insight into the processability of the prepreg. It answers questions about processing factors such as: out-time; excessive bleeding; exotherms; or void formation due to out-gassing.

#### 3.2.1 Thermal Analysis, TGA and DSC

The volatiles content and the high temperature weight loss of the material were determined by standard thermogravimetric Analysis (TGA) using the Dupont 990 Thermal Analyzer (controller) interfaced with a 951 Thermal Gravimetric Analyzer. The heat of reaction and the temperature of onset of the reaction were determined by differential scanning calorimetry (DSC) using the Dupont 910 DSC interfaced with the 990 Thermal Analyzer. The TGA was run from RT to 680°C at 10°C/min in a nitrogen atmosphere and the DSC was run from RT to 400°C at 10°C/min. This information was used as a qualitative assessment of the proposed cure cycle, not in order to optimize the cure cycle.

#### 3.2.2 Rheological Characterization

AT monomers typically have high initial melting temperatures (up to 100°C) that make prepreg handling difficult. Extensive rheological characterization was done with the prepreg to determine what the behavior of the CATB-44 resin was. The modified resin was a two-

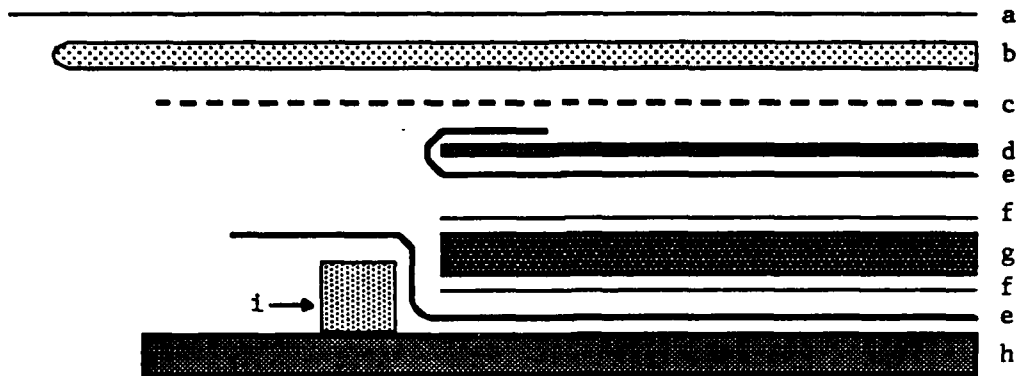
phase system with an inverted phase morphology. The chemorheology of multiple phase systems is quite complex, so this extension of the basic evaluation was justified. American Cyanamid provided neat resin samples for characterization and comparison to the composites. In addition, T-300/CATB-44 flex specimens were swollen in MEK, acetone, and methylene chloride to determine the sensitivity of the second phase to solvents.

### 3.3 Composite Panel Fabrication

#### 3.3.1 Handling, Processing

The CATB-44 resin had a  $T_g$  above room temperature so the prepreg was dry and "boardy." It split easily and could not be handled at all while still cold. The prepreg roll was allowed to warm up and a heat source such as a hot air gun or soldering iron was used to "tack" together the prepreg during lay-up. In addition, extreme care had to be used in handling large unidirectional lay-ups as they can easily break irreparably apart.

The CATB-44 prepreg was always stored below 0°C to prevent advancement of the resin. The CATB-44 prepreg has a softening temperature of about 30°C, so out-time was not a problem with this resin system. The resin content of the prepreg was determined, through resin extraction with MEK as the solvent, to be  $33.1 \pm 1.3\%$ . This resin content was considered to be "net resin" for the composite, so we did not anticipate bleeding during cure. The bagging used is shown in Figure 2. The bagging technique was essentially the same used for all "Net Resin/Low Bleed"-type materials. The cure cycle employed was the one recommended by American Cyanamid. Their cure cycle is given in Table 2. The cure cycle is not optimized, as evidenced by the long postcure. The cure cycle, however, does give the expected reproducible mechanical properties and stays within the range of conventional epoxy cure conditions.



- a. Non-porous nylon film
- b. Nylon matted bleeder ply
- c. Perforated nylon film
- d. Aluminum top caul plate
- e. Non-porous teflon coated fiber glass cloth
- f. Porous teflon coated fiber glass cloth
- g. CATB-44/T-300 uncured laminate
- h. Aluminum bottom caul plate
- i. Si-rubber dam

Figure 2. Bagging diagram for T-300/CATB-44 laminate.



Table 2. CATB-44 Cure Cycle.

Event	T.time.rate	Pressure
Heat from RT to Hold Temp	3°C/min	30" Vac. + 85 psi
Hold Temperature	150°C, 90 min	30" Vac. + 85 psi
Heat from Hold to Cure Temp	3°C/min	30" Vac. + 85 psi
Cure Temperature	177°C, 240 min	No Vac. + 100 psi
Cooldown from Cure Temp	3-5°C/min	No Vac. + 100 psi
Postcure	250°C, 240 min	free-standing, in air

### 3.4 Composite Mechanical Properties Evaluation

#### 3.4.1 Sample Preparation

Table 3. gives the specific dimensions of the samples used for the tests outlined in Table 1. The specimens were cut from cured panels using a water-cooled diamond impregnated abrasive saw. The specimens were then trued to within 0.001 in/in parallel using a high-speed router with an abrasive bit. If necessary, the specimen edges were then polished using increasingly finer grades of wet abrasive paper. Specimens were then dried in a convection oven at 100°C for several hours and then stored in a cabinet desiccator until tested. The group of test specimens to be used for water absorption studies were selected at random from these dried specimens and then weighed. The average weight gain plotted versus the square root of time is shown in Figure 3. It took approximately 2 weeks for the weight gain to equilibrate. The SBS and the  $[\pm 45]_2S$  coupons had disproportionately higher weight gains than the flexural coupons. The  $[\pm 45]_2S$  probably gained more water due to the epoxy/fiber glass endtabs that were bonded in place prior to water exposure. Since these samples did not equilibrate in the 2-week period we assumed that the T-300/CATB-44 had equilibrated and the additional weight gain was due to the endtabs. The SBS specimens may have acquired micro-cracks during the cutting and edge polishing operations. They were then placed in a sealed beaker of distilled water and placed in

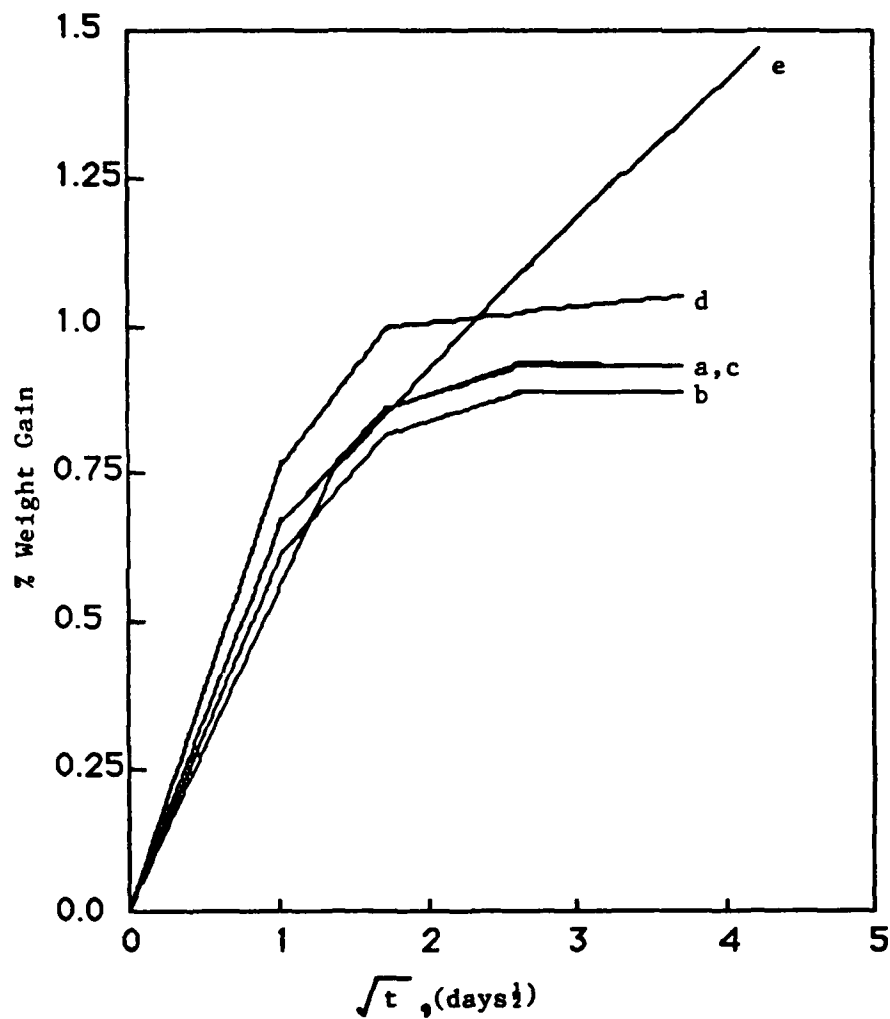


Figure 3. Water absorption of T-300/CATB-44 composite. a,b, and c are flex coupons. d indicates SBS coupons. e indicates IPS coupons end-tabbed with epoxy/fiber glass tabs.

an oven at 70°C (158°F). After 24 hours, and then after increasingly longer time intervals, the samples were removed, dried of surface moisture and weighed. They were then immediately re-immersed in the water and placed back into the oven. Care was taken to completely dry off samples, and measurements were made quickly enough so that water desorption was not a problem. Measurements were taken until the weight gain became a constant. The samples were then kept in distilled water at room temperature until testing. At elevated temperatures (350°F) the temperature was only permitted to equilibrate for approximately 3 minutes to minimize moisture loss.

Small sections (~0.25" x 1.0") were cut from various locations in each panel for photomicrographs. The sections were mounted in an epoxy plug with the fibers running perpendicular to the bottom surface. This provides an "end view" of the composite cross section. The hardened epoxy was then polished using successively finer grades of wet abrasive paper and finished to a highly polished surface with an alumina polishing compound.

Table 3. Test Sample Dimensions.<sup>a,b</sup>

Test	ASTM	L	W	Th
0° 3-Pt Flexure	D790-81	3.0	0.5	0.06
0° 4-Pt Flexure	D790-81	3.0	0.5	0.06
90° 4-Pt Flexure	D790-81	3.0	0.5	0.06
0° 4-Pt Shear	D790-81	3.0	0.5	0.06
0° SBS	D2344	1.0	0.25	0.06
0° Tension	D3039-76	9.0	1.0	0.06
In-Plane-Shear	D3518-76	12.0	1.0	0.04
Edge Delamination		9.0	1.0	0.06
Double Cantilever Beam	D30.02	9.0	1.0	0.12 <sup>c</sup>
End Notched Flexure	D30.02	6.0	1.0	0.12 <sup>c</sup>

<sup>a</sup>ASTM reference is to relevant document.

<sup>b</sup>All units are inches

<sup>c</sup>Denotes a 1.5" KAPTON™ strip was placed along mid-plane.

### 3.4.2 Mechanical Characterization

#### 3.4.2.1 4-Point, 3-Point, SBS Mechanical Testing.

The 4-Point flex and shear testing were performed on an INSTRON 1123 table-top load frame in compression. A detailed drawing of the 4-Point fixture used is given by Carlin (1988). The 90° 4-point flex tests at room temperature were performed using a strain gauge attached to the tensile face to measure strain. The 3-Point flex testing and Short Beam Shear (SBS) were done on an INSTRON TTS load frame in tension. Detailed drawings of the 3-Point and SBS loading fixture are given elsewhere (Carlin, 1988). The 4-Point, 3-Point, and SBS tests were all run at a crosshead displacement rate of 0.05"/min. The strengths and moduli from these experiments are calculated using linear elastic beam theory. Derivation of the equations can be found in any mechanics of solids textbook, so it will suffice to simply give the equations here. Table 4 gives the equations used to calculate the appropriate flexural strength and modulus properties.

Table 4. 4-Point, 3-Point, and Short Beam Shear Mechanical Properties Equations.

Property	3-Point	4-Point (1/4-Pt)
$\sigma_{\max}$ , crosshead disp.	$3PL/(2bt^2)$	$3PL/(4bt^2)$
$\tau_{\max}$ , crosshead disp.	$3P/(4bt)$	$3P/(4bt)$
$E_{\text{flex}}$ , crosshead disp.	$(dP/du)L^3/(4bt^3)$	$(dP/du)L^3/(8bt^3)$
$E_{\text{flex}}$ , strain gauge	N/A	$(dP/d\epsilon)L/(bt^2)$

In these equations the symbols have the following meanings:

P = maximum load;

L = support span;

b = specimen width;

t = specimen thickness;

dP/du = slope of load-crosshead displacement curve;

and dP/d $\epsilon$  = slope of load-strain curve.

### 3.4.2.2 0° Tension, Edge Delamination, and In-Plane Shear Mechanical Testing.

The 0° tensile, IPS, and ED strengths of the T-300/CATB-44 composite were measured on an INSRON TTC universal testing machine in tension. The strain of the 0° tension and the ED specimens was measured using a high-strain magnification extensometer while the longitudinal and transverse strain of the IPS specimens was measured with strain gauges. The 0° tensile strength and modulus are calculated using the following relationships:

$$\sigma_{\max} = P/bt \quad E = dP/d\epsilon \ 1/bt, \quad (1)$$

where the symbols all have the same meaning as before.

The in-plane shear modulus,  $G_{12}$ , of the IPS specimens is determined using the following relationship:

$$G_{12} = P/2(\epsilon_1 - \epsilon_2)bt \quad (2)$$

where  $G_{12} = \tau_{\max}/\nu$ ,  $\tau_{\max} = \sigma_{\max}/2$ ,  $\nu = \epsilon_1 - \epsilon_2$ .  $\nu$  is Poisson's Ratio and  $\epsilon_1, \epsilon_2$  are the longitudinal and transverse strains respectively.

### 3.4.2.3 Double Cantilever Beam (DCB) and End Notched Flexure (ENF) Mechanical Testing.

One of the important properties of aerospace composites is the interlaminar fracture toughness. It can be measured using a variety of test methods and geometries. The T-300/CATB-44 interlaminar fracture toughness was measured in two modes. These were Mode I, the so-called DCB geometry, and Mode II, the ENF geometry. The method used in our laboratory for the DCB test has been described elsewhere (Whitney et al., 1982) so I will only give the equations that are used to calculate  $G_{IC}$ , the Mode I interlaminar fracture toughness. The three common methods are known as the Area

Method, Beam Theory Method, and Empirical Method. The following equations are used in these three cases:

Area Method:  $G_{IC} = (1/2b\Delta a) (P_{i-1}\delta_i - P_i\delta_{i-1}),$  (3a)

where  $b$  = beam width,  
 $\Delta a$  = change in crack length,  
 $P_i$  =  $i$ th load reading,  
 $\delta_i$  =  $i$ th deflection reading.

Beam Theory:  $G_{IC} = 3P_c\delta_c/2ba,$  (3b)

where  $P_c$  = load reading,  
 $\delta_c$  = deflection reading,  
 $a$  = crack reading.

Empirical Method:  $G_{IC} = nP_c\delta_c/2ba$  (3c)

where  $n$  is from a power-law fit of  $\delta = RPa^n$ . " $n$ " is the slope of  $\log(P/\delta) = -\log R - n \log a$ .

The ENF method of determining interlaminar fracture toughness is now in ASTM Round Robin testing (ASTM 30.02) and those instructions for testing and data analysis were used in this investigation. The specimen geometry and dimensions used are given in Figure 4. The pre-cracked beam is loaded in a 3-Point fixture with load and support pin diameters of 0.125" to 0.375". Testing machine compliance is assumed to be negligible in this analysis, but may be incorporated into the analysis if deemed necessary. Two methods were used to analyze the data. The first is based on beam theory and is given by the following relationships:

$$G_{IIC} = 9a^2P_c^2(C_T - C_s^*)/2b(2L^3 + 3a^3), \quad (4)$$

where  $C_T = [(2L^3 + 3a^3)/8Ebh^3] + [(1.2L + 0.9a)/4bhG_{12}],$

and  $C_s^* = [1.2L + 0.6a - (0.2L^3/a^2)]/4bhG_{12}.$

The symbols used have the following meanings:

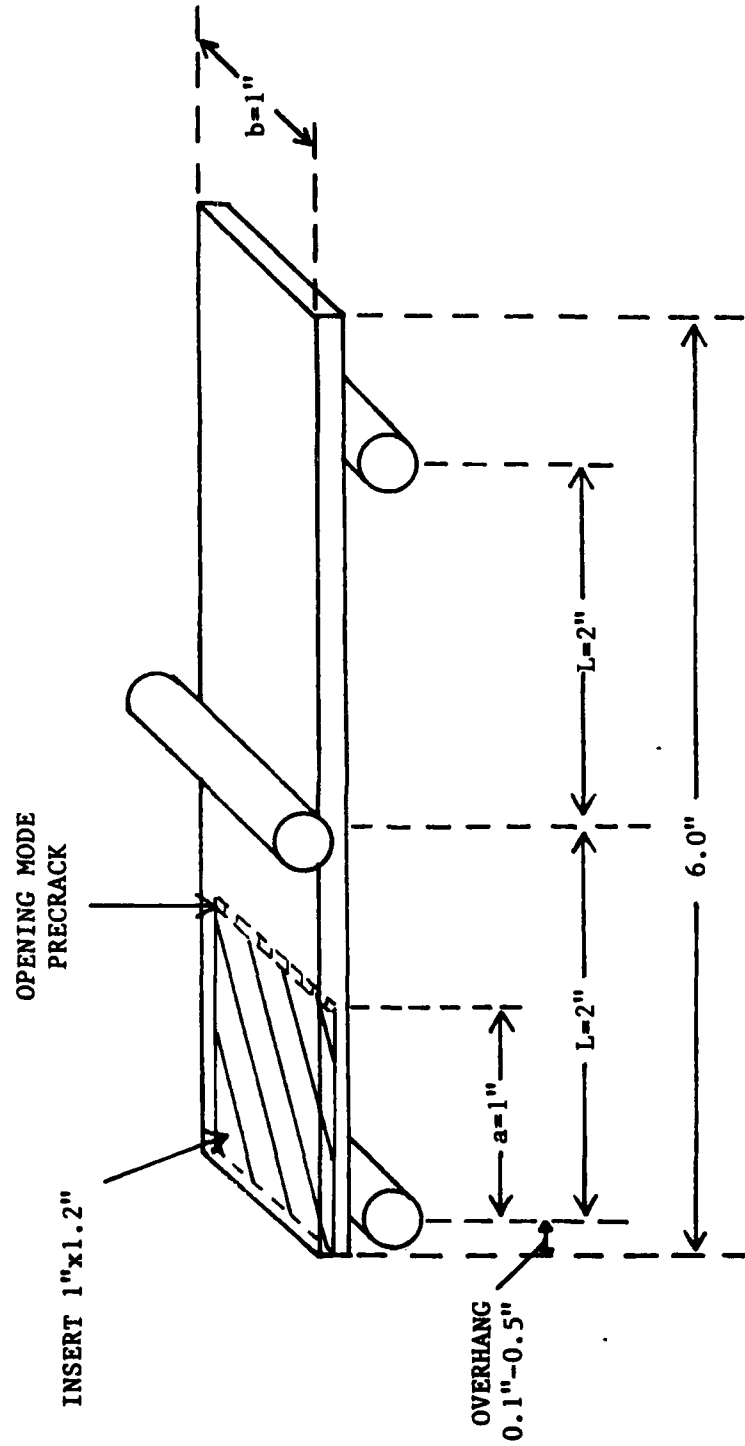


Figure 4. Schematic diagram of End Notched Flexure test specimen.

$G_{IIC}$  = Mode II interlaminar fracture toughness

$C_T$  = beam flexural compliance

$C_s^*$  = modified shear compliance

$P_c$  = critical load;

$L$  = span of support fixtures;

$E$  = Young's Modulus;

$a$  = crack length;

$b$  = beam width;

$h$  = beam thickness;

and  $G_{12}$  = in-plane shear modulus.

The second method used to calculate the Mode II interlaminar fracture toughness uses an empirical linear fit of the specimen flexural compliance as a function of crack length cubed and is given by the following expressions:

$$G_{IIC} = 3P_c^2 m a^2 b_o / 2b^2. \quad (5)$$

Where  $C_T = m a^3 + \text{constant}$ ,  
 $b_o$  = specimen width used for compliance calibration,  
and  $m$  = slope of line describe above.



## SECTION 4. RESULTS and DISCUSSION

### 4.1 Thermal Characterization

#### 4.1.1 Thermogravimetric Analysis, TGA

The TGA scan of the T-300/CATB-44 prepreg is shown in Figure 5. The scan indicates there are two weight loss mechanisms. The lowest-energy mechanism occurs at approximately 235°C and results in 2% weight loss. The second occurs at approximately 445°C and results in an additional 16% weight loss. The cure cycle holds are at 150°C and 177°C respectively, so the volatilization at 235°C should not be a source for void formation. The origin of the 2% loss is not known. It could be associated with the second-phase toughening, a residual solvent, a or reaction by-product.

The TGA scan of the fully cured and post-cured panel is shown in Figure 6. The scan shows that the fully cured panel has only one weight loss peak at 448°C. The weight loss is approximately 20%. Interestingly, the combined weight losses of the two peaks in the prepreg TGA scan is also approximately 20%. This is evidence that the first peak could be a lower molecular weight species of m-ATB while the second loss could be associated with oligomeric forms of ATB. The weight losses are apparently due to reaction of an intramolecular moiety since the total weight loss is unaffected by curing. The chemical nature of the second phase must be similar to the ATB since the weight loss of pure ATB was reported by Dynes (1985) to occur at the same temperature. If the second phase was chemically different we would expect to see some weight loss at another temperature.

#### 4.1.2 Differential Scanning Calorimetry, DSC

The DSC scan of the T-300/CATB-44 prepreg is shown in Figure 7. There is a large endotherm between 20°C and 30°C typically seen during DSC scan start-up. The resin is also melting in this range and is obscured by the start-up endotherm. Pure ATB has a melting point

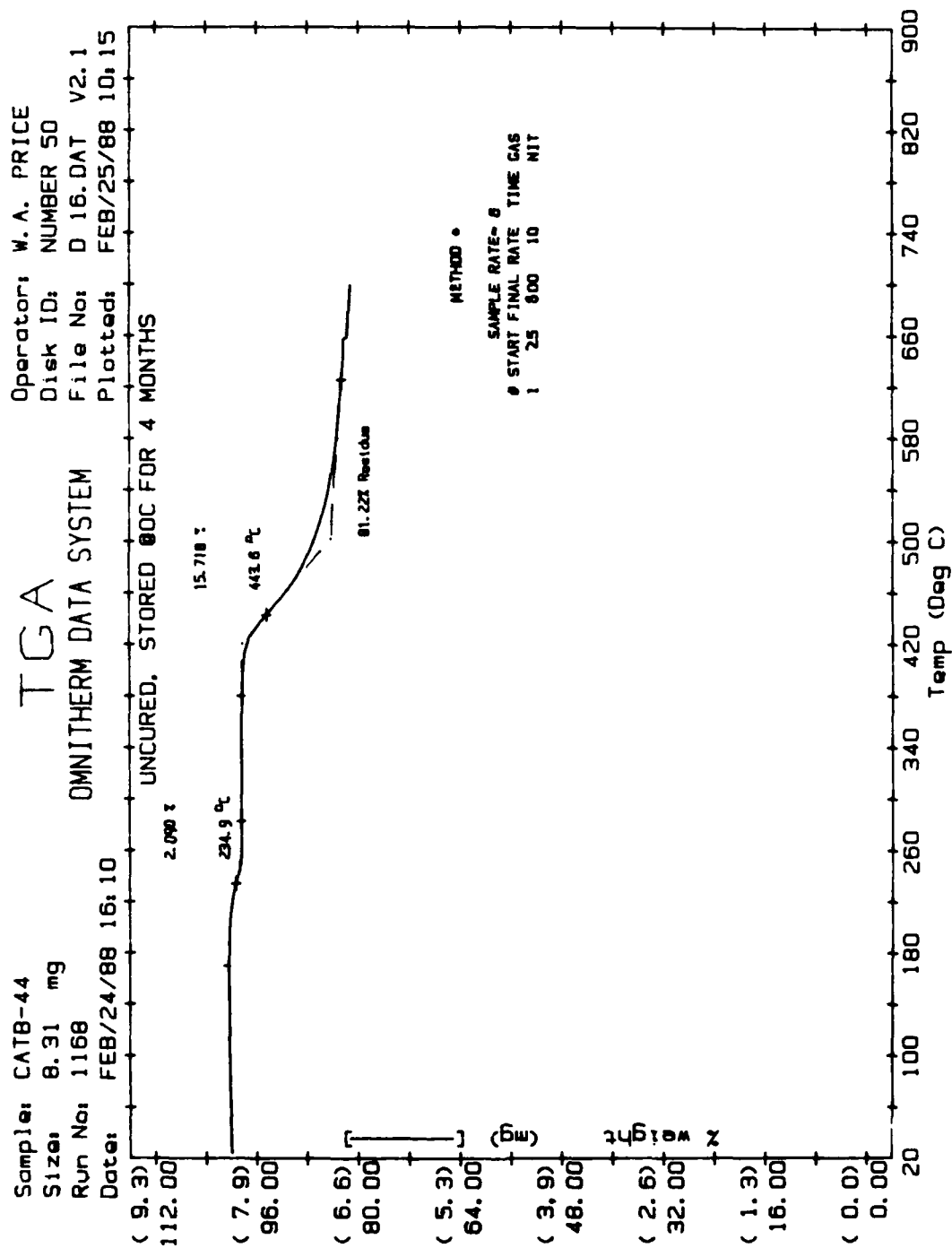


Figure 5. TGA scan of T-300/CATB-44 prepreg.

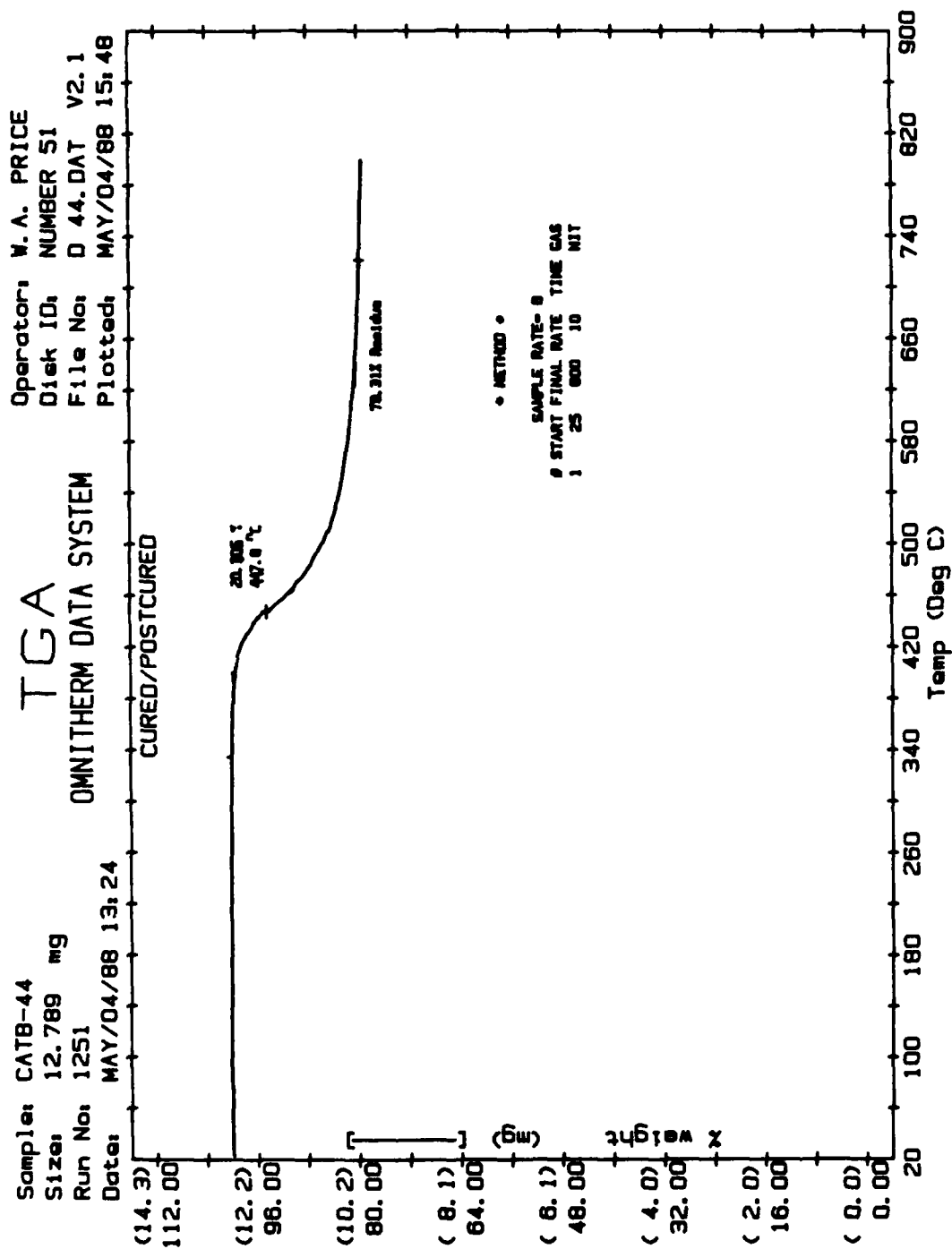


Figure 6. TGA scan of a fully cured T-300/CATB-44 composite.

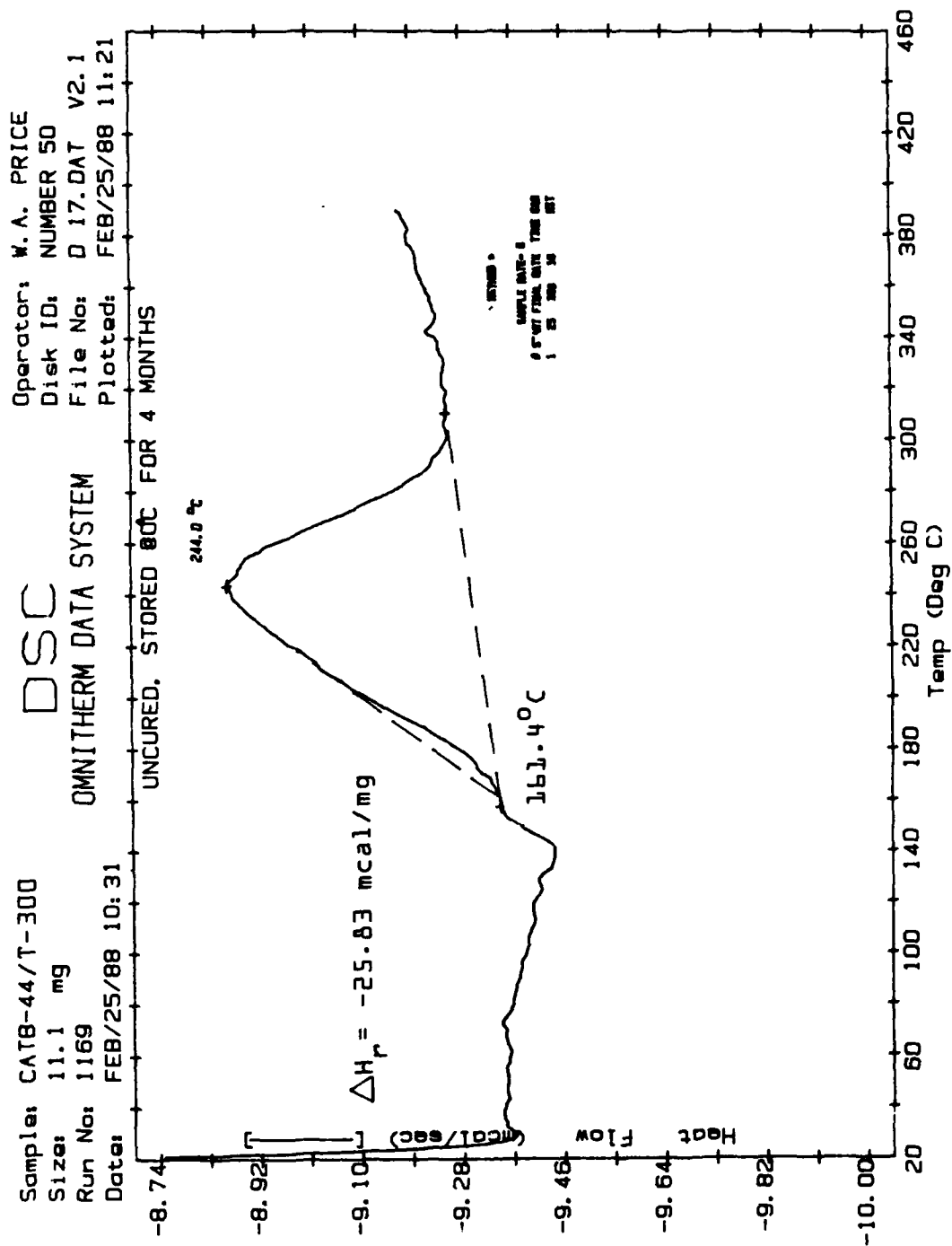


Figure 7. DSC scan of T-300/CATB-44 prepreg.

of approximately  $-10^{\circ}\text{C}$  (American Cyanamid , 1988). The higher melt temperature indicates that the monomer has probably undergone some reaction to increase its molecular weight. The only other feature of the scan is a major exotherm beginning at  $160^{\circ}\text{C}$  and peaking at  $244^{\circ}\text{C}$ . The integration of this peak gives a heat of reaction of 25.83 mcal/mg.

The DSC scan of the fully cured and postcured panel is shown in Figure 8. There are no significant endotherms or exotherms visible. From this we can assume that the panel was completely cured and free of absorbed moisture.

The peak temperature of the reaction exotherm shown on the curve in Figure 7 corresponds closely to the peak temperature of the 2% weight loss of the prepreg TGA scan. The slight temperature difference may be accounted for by the fact that the TGA and DSC scans are nonisothermal experiments and are performed on different instruments. Due to variations in thermal mass, sensor location, sensor accuracy, and sample mass, a  $10^{\circ}\text{C}$  difference is considered negligible. Both the DSC and the TGA scan were performed at  $10^{\circ}\text{C}/\text{min}$  under nitrogen so the TGA weight loss seems to be associated with the polymerization reaction. The radical addition reaction of the AT resins does not have any volatile products. There are thus two possible reasons why the temperatures may correspond. First, the 2% weight loss could be associated with an impurity that vaporizes at  $\sim 240^{\circ}\text{C}$  and its heat of vaporization is lost in the heat of reaction exotherm peak. The second possibility is that the second phase formulation by American Cyanamid does involve production of a volatile by-product. If this is the case, we would expect that the rate of weight loss, i.e., the first derivative of the weight loss versus temperature curve, should have the same distribution as the rate of reaction DSC curve.

Figure 9 shows the rate of weight loss versus temperature compared to the actual weight loss curve. The discrete noise level in the derivative is because the derivative is calculated by differences of

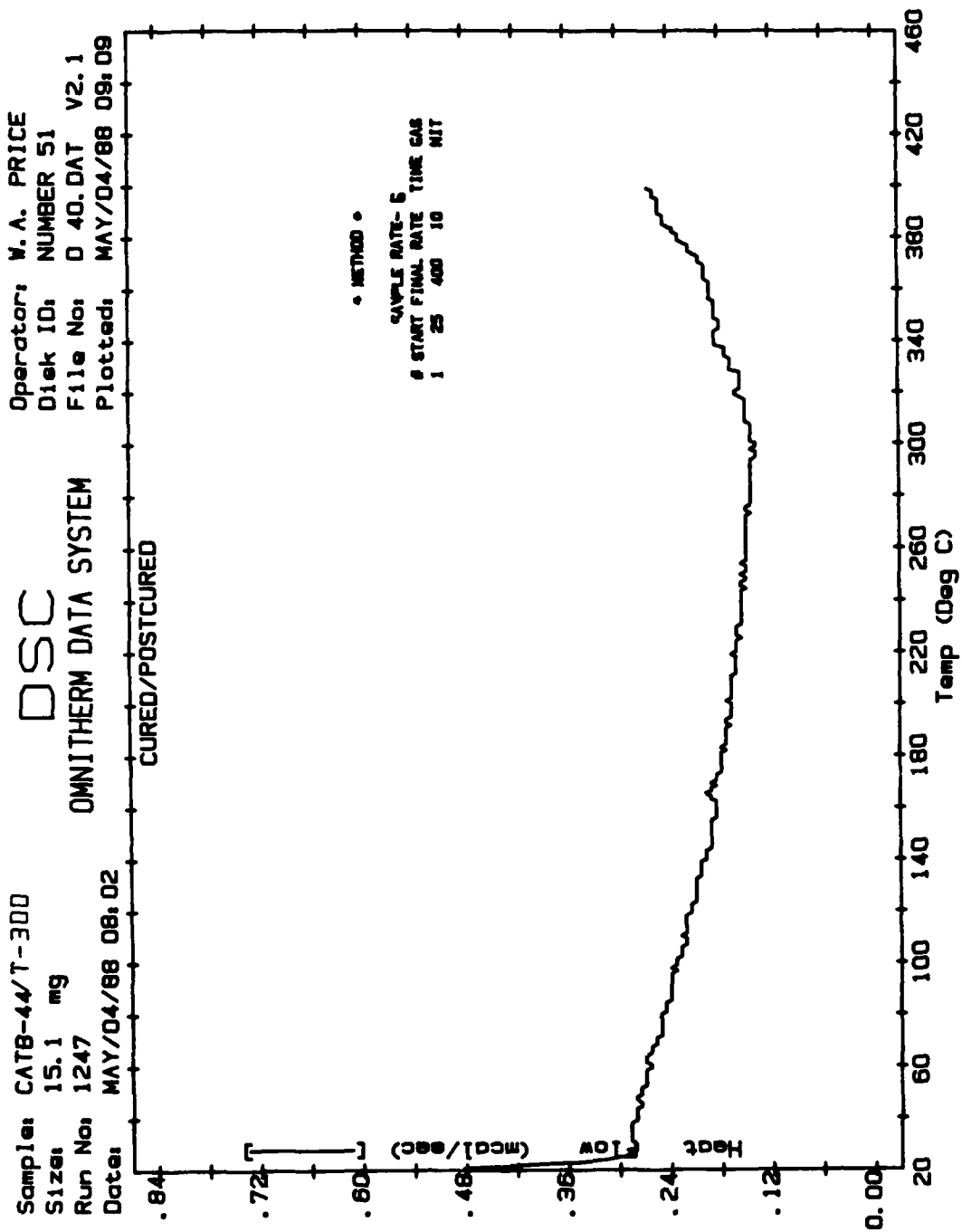


Figure 8. DSC scan of fully cured T-300/CATB-44 composite.

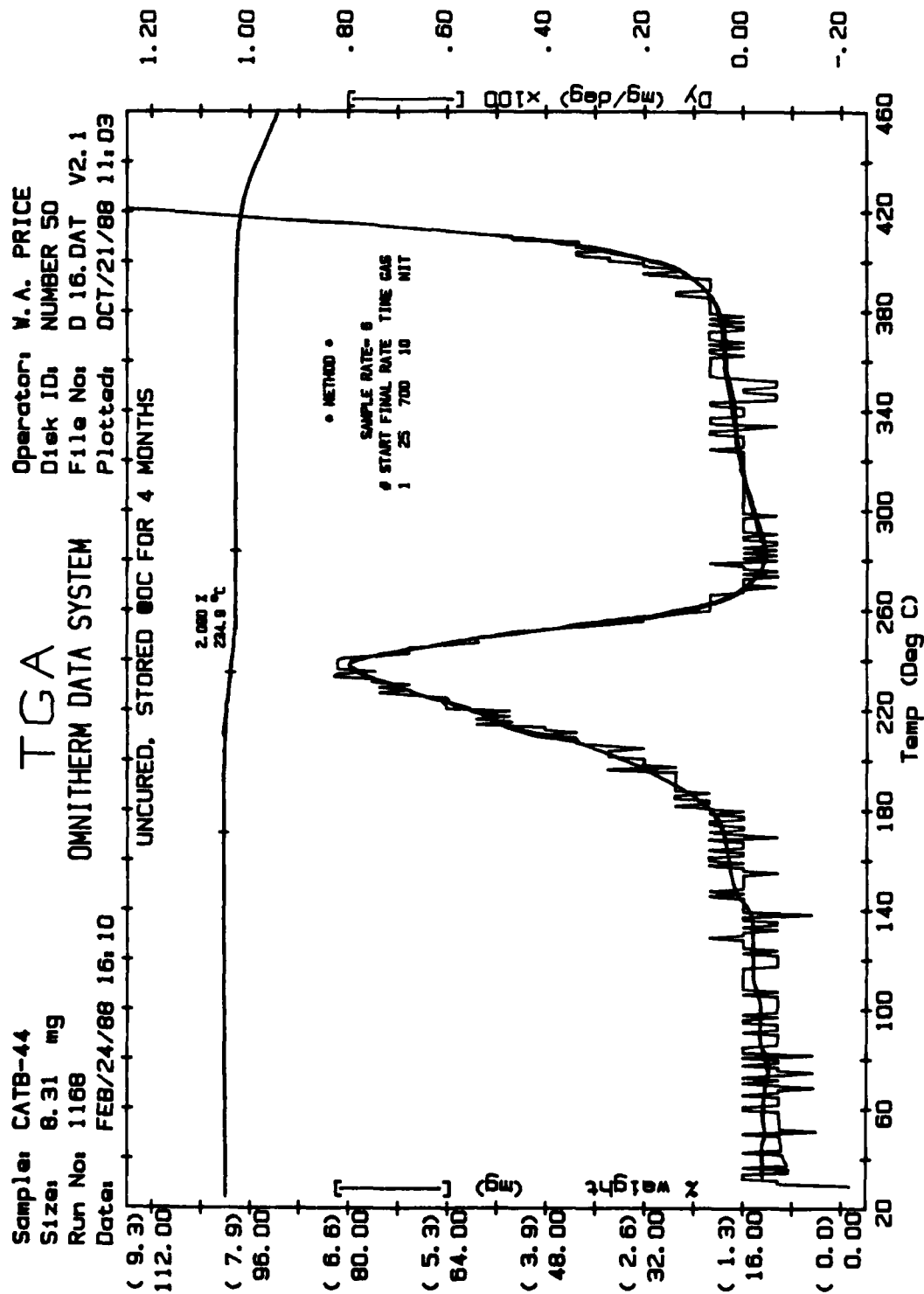


Figure 9. TGA and d(weight loss)/dT of T-300/CATB-44 prepreg.

data with a finite resolution. The smoothed line through the derivative data shows that the peak has an "induction" period similar to the DSC peak of Figure 7. The peak is centered around 240°C and then drops off abruptly.

Figure 10 shows the DSC and the TGA derivative peak superimposed by plotting on the same temperature scale. In spite of the differences between the two instruments there appears to be a good correspondence between the two peaks. The peaks occur at approximately the same temperature and the shape of the TGA curve has similar features as the DSC curve. This is strong evidence that the weight loss corresponds to some by-product of reaction of the CATB-44 resin.

## 4.2 Rheological Characterization

### 4.2.1 Dynamic Mechanical Analysis, DMA

#### 4.2.1.1 DMA of Prepreg

The DMA scan of a  $[0]_{12}$  0.5" x 2.5" prepreg laminate is shown in Figure 11. The laminate is heated at 2°C/min under nitrogen to well above its cured  $T_g$ . This is termed a "cure scan" since it is a measure of the viscoelastic nature of the resin as it is curing. The storage modulus curve has several transitions. The first transition occurs on the heat up just above room temperature. This is the melting of the CATB-44 precursors. The uncured modulus of the prepreg is of the same order of magnitude as the fully cured composite. This, in part, explains why the prepreg is so difficult to handle. The next transition occurring at approximately 130°C, is apparently another melting transition. It corresponds to a slight endotherm in the DSC scan in Figure 7. This is probably associated with the presupposed oligomeric forms of ATB present. Two distinct melting transitions is strong evidence that the CATB-44 resin has a bi-nodal molecular weight distribution. The next transition is the large (3 orders of magnitude change) increase due to the onset of the curing reaction that begins around 200°C. On the



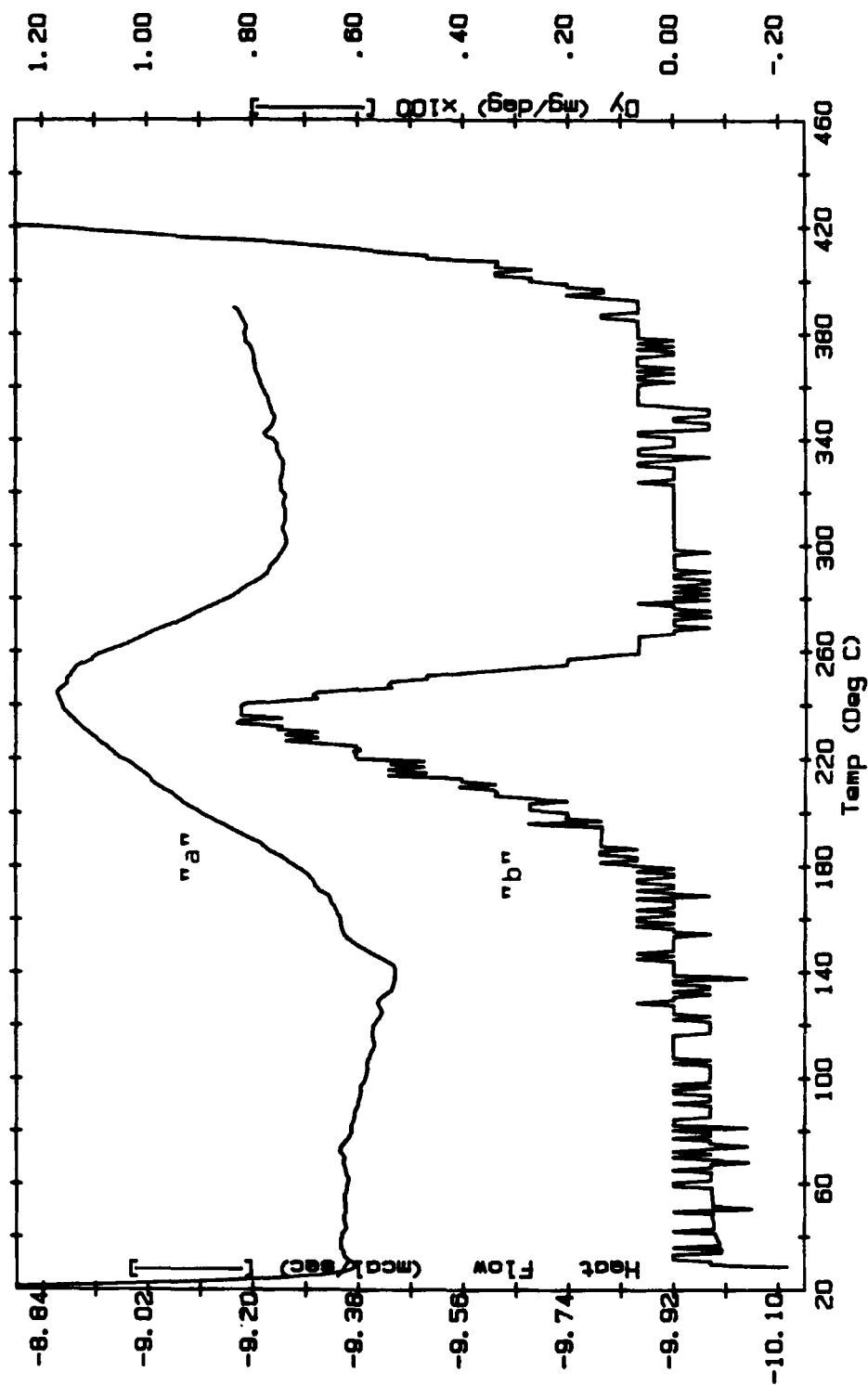


Figure 10. DSC and d(weight loss)/dT curves for T-300/CATB-44 prepreg. Curve "a" is DSC scan from Figure 4. and curve "b" is from TGA scan in Figure 9.

CURE STUDY CATB-44. A. 2 D. CURLISS 2-26-88

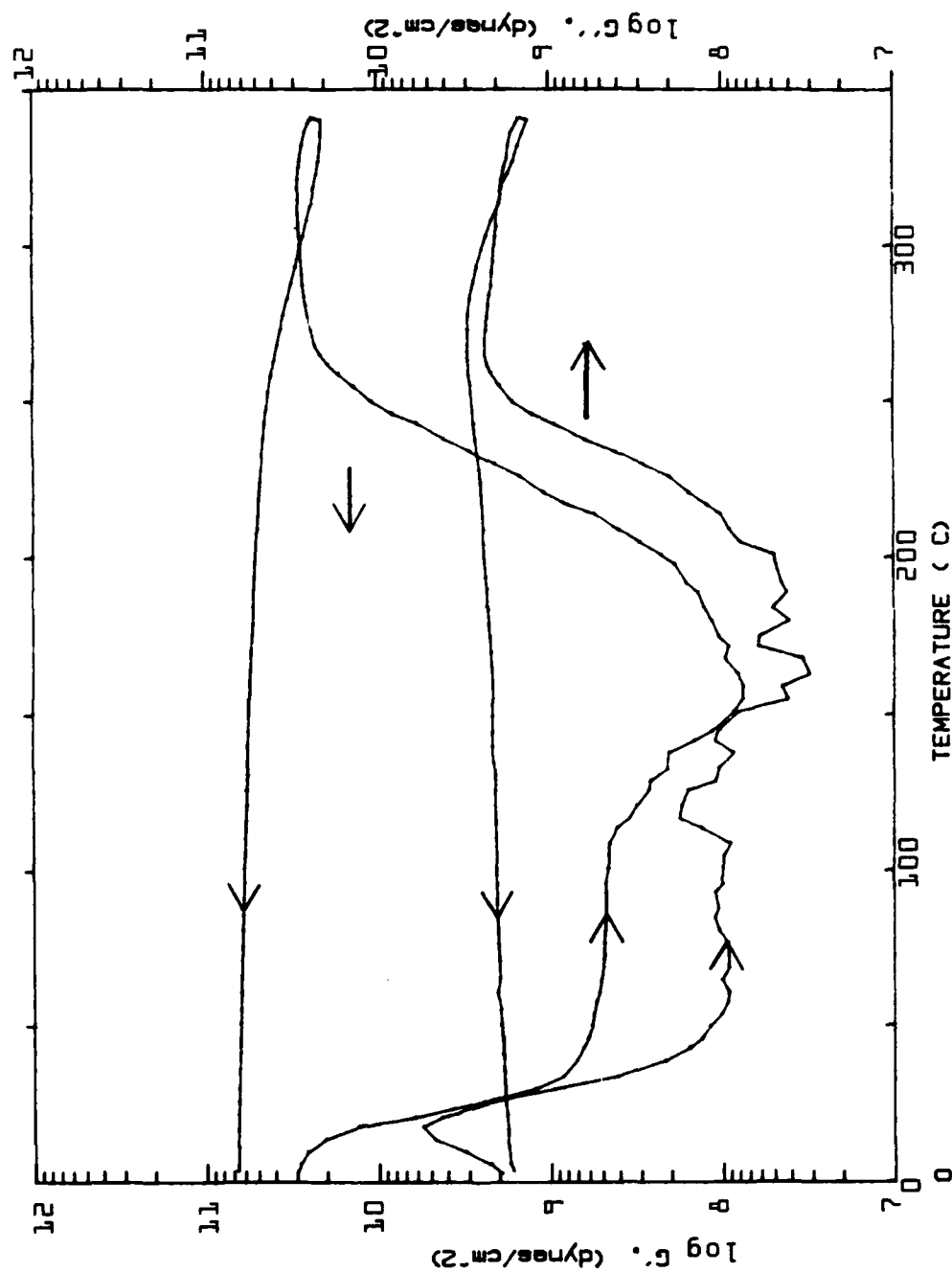


Figure 11. Dynamic Mechanical Analysis (DMA) of uncured T-300/CATB-44 prepreg. Heating rate was 2°C/min.

cool-down the material passes through its glass transition at approximately 260°C. Below this temperature its behavior is dominated by the storage modulus and it is very nearly independent of temperature.

In order to further understand the nature of the second melting a test was devised in which the material was heated to above 150°C at 5°C/min and then quenched to room temperature. By heating to 150°C we have passed through both melting transitions at a rate that should prevent any extent of cure. Figure 12 shows the results of this heat/quench/reheat cycle. The mechanical behavior during the first heating is essentially the same as is shown in Figure 11. However, upon subsequent reheating the initial melt is moved to a slightly higher temperature and occurs over a wider temperature range. The second melt that occurs at 130°C in the initial prepreg is now absent! This indicates that the second melt is due to a crystalline phase that has the same amorphous melt temperature as the initial lower melt temperature component. In other words, this is further evidence that the two melts are due to CATB-44 precursors that are similar in chemical nature, but may be of different molecular weight.

#### 4.2.1.2 DMA of Cured CATB-44 Resin and T-300/CATB-44 Composite

American Cyanamid (1988) reported that the neat resin is an inverted two-phase morphology. This was confirmed by this study (see paragraph 4.5.1). We would expect two glass transitions if this is the case. The storage and loss modulus was measured for both the neat resin and a fully cured T-300/CATB-44 composite. The results are shown superimposed in Figure 13. The neat resin and the composite both show the ATB glass transition at approximately 250°C and also a sub-T<sub>g</sub> relaxation centered at about -100°C. However, in addition the neat CATB-44 has a sub-T<sub>g</sub> transition at just over 100°C. This may be the glass transition of the continuous phase in the neat resin. One method that could be used to verify if indeed that 100°C transition was the glass transition of the second

cure study catb-44. a. 3

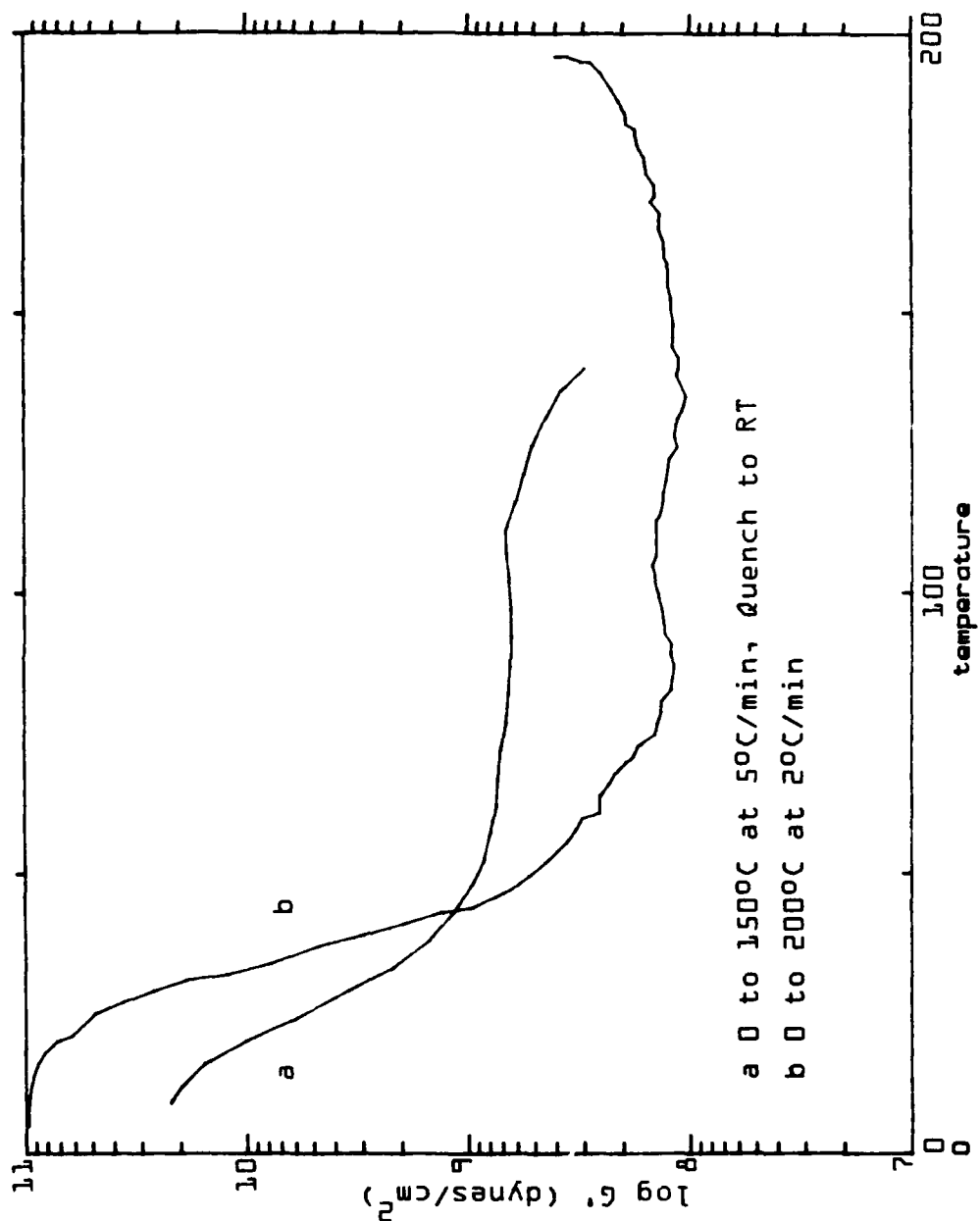


Figure 12. Shear storage modulus of T-300/CATB-44 prepreg during Heat/Quench/Reheat cycle.

CATB-44 NEAT RESIN TEMP SCAN 22 APR 88 D. CURLISS

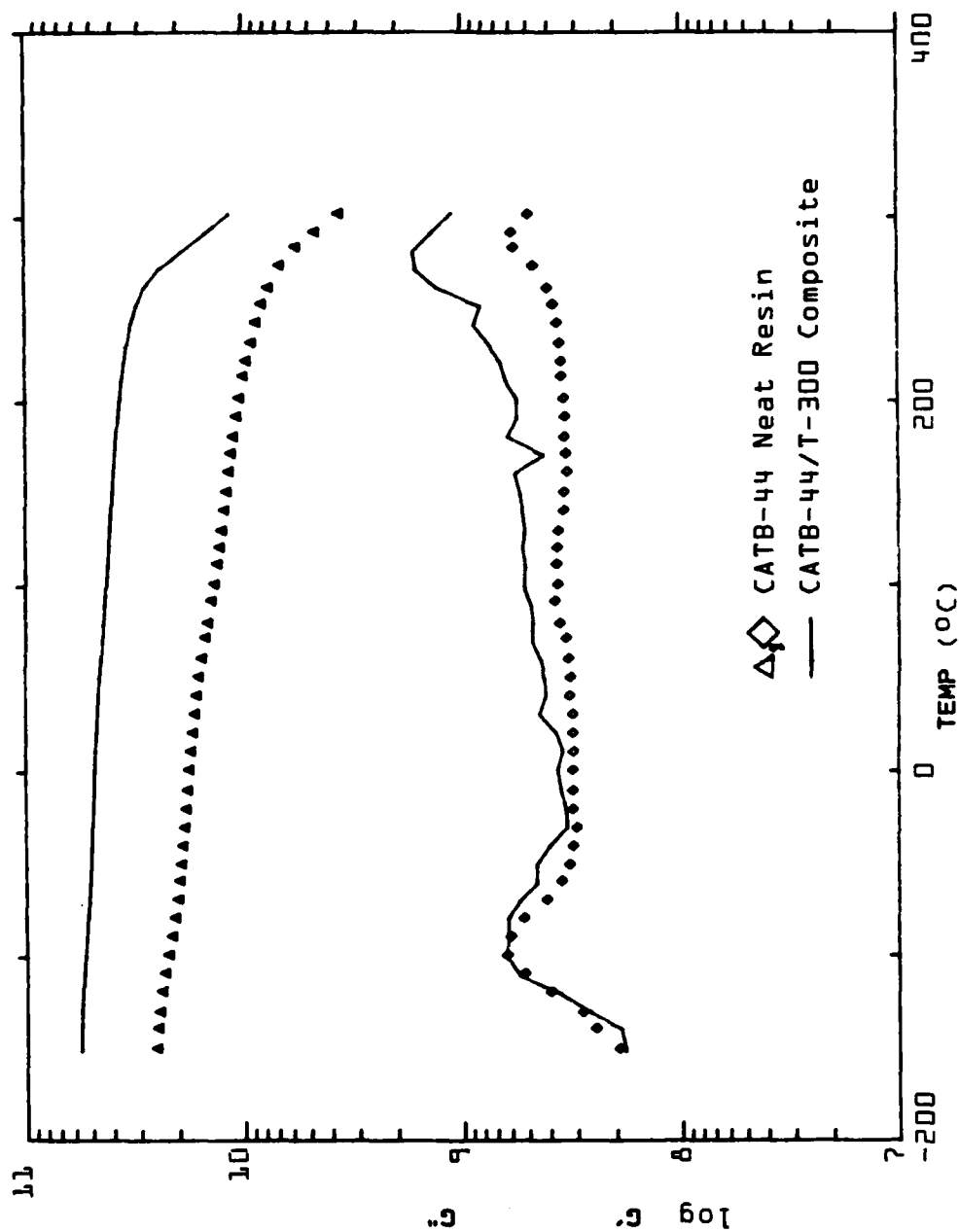


Figure 13. Shear storage and loss modulus at 1Hz for CATB-44 neat resin and for T-300/CATB-44 composite.

phase would be to perform creep studies on the neat resin around the 100°C temperature range. If the second phase is truly undergoing its glass transition and not just another sub-T<sub>g</sub> relaxation we would expect dramatic changes in the creep behavior. The material would behave as if it were a filled rubber, rather than a two-phase glassy polymer.

#### 4.3 Microscopic Evaluation

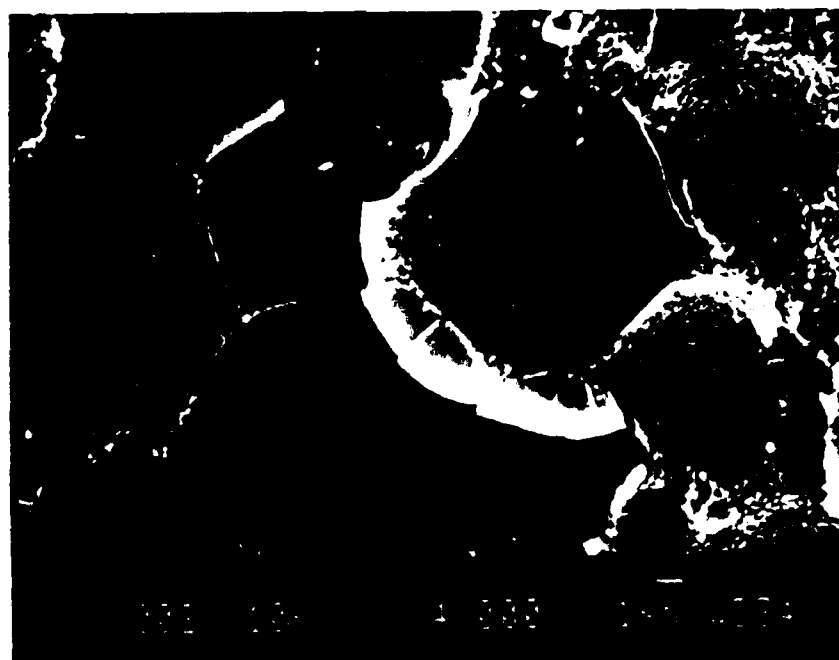
##### 4.3.1 Scanning Electron Microscopic (SEM) Evaluation

SEM photographs were taken of a neat resin fracture surface. The photographs in Figures 14a and 14b clearly demonstrate the two-phase nature of the modified ATB. The morphology is an inverted two-phase structure since the toughening phase is continuous and the discrete nodules are the brittle phase. The nodules have smooth crack propagation surfaces typical of brittle glassy polymers. The regions separating the nodules appear to have undergone a great deal of ductile deformation. However, the failure surface appears to have passed through several of the brittle nodules in the same plane. This would indicate that the continuous phase was not very effective at dissipating energy through a large deformation mechanism or through blunting and diverting the crack front.

The inverted two-phase morphology has inherent problems that could be serious drawbacks to its use as an aerospace structural resin. These problems arise from the fact that the highly temperature and moisture resistant ATB is no longer what is exposed to the environment. The toughening phase is the "glue" that holds the ATB particles together and therefore its properties will be the limiting factor in the applications for the formulated resin. To test this hypothesis, several swelling studies were performed on the T-300/CATB-44 composite in the common solvents MEK, acetone, and methylene chloride. If the continuous phase were susceptible to these it should show up as a large weight gain. In fact, the weight gain in these solvents was far less than the moisture pickup shown in Figure 3. This indicates that the continuous phase is probably a thermosetting material with very good solvent resistance like the ATB itself.



(a)



(b)

Figure 14. SEM photographs of CATB-44 neat resin compact tension fracture surface.

SEM photographs of the composite fracture surfaces revealed features similar to those described by Dynes (1985) for the pure AS-4/ATB composite. Figures 15a and 15b are of a Mode I fracture surface. Photograph "a" shows that there are many "clean" fibers and impressions of fiber pull-outs indicating poor interfacial adhesion of the matrix to the fiber.

The same inverse two-phase morphology of the resin is not observed in the composite. The nodules of the neat resin are approximately 5 to 10  $\mu\text{m}$  in diameter. This is smaller than the interfiber spacing in the composite, so it is not clear if the nodules are present in the composite in a different distribution or if they do not form because of the fiber presence.

#### 4.3.2 Photomicrograph Evaluation (PMG)

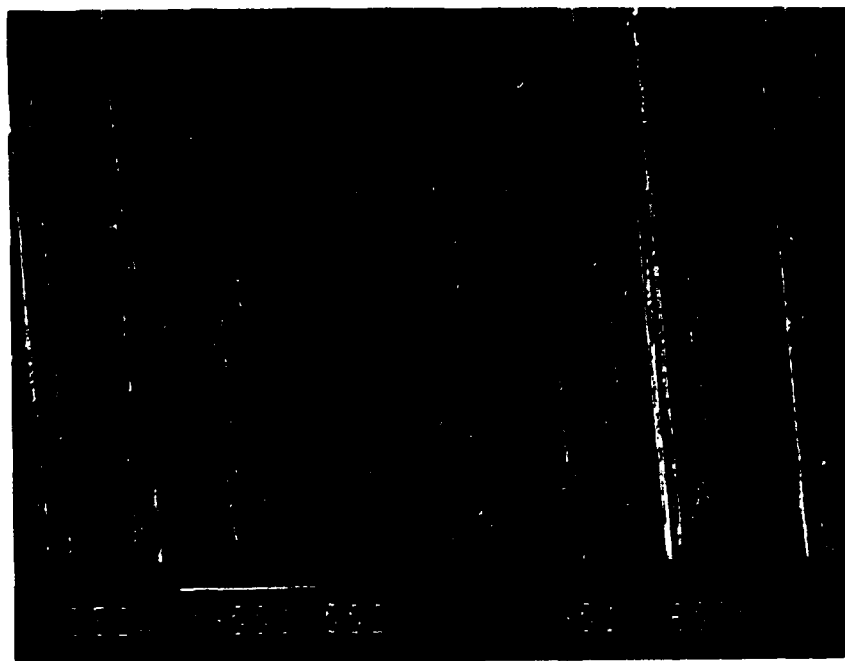
PMGs were taken of every T-300/CATB-44 panel to check fiber distribution, porosity, and also micro-cracking. Figures 16a-16c shows example PMGs of  $[0]_{12}$ ,  $[\pm 45]_{2S}$ , and a  $[\pm 30, +30, 90_2]_S$  panel respectively. The PMG of the unidirectional and of the  $[\pm 45]_{2S}$  panel show good fiber distribution with some resin rich areas between plies, but no evidence of micro-cracking. The  $[\pm 30, +30, 90_2]_S$  laminate, however, had several micro-cracks in the  $90^\circ$  center plies. The micro-crack shown in the PMG traverses the entire  $90^\circ$  section. Several other cracks were noted that did not traverse all of the  $90^\circ$  plies.

### 4.4 Mechanical Properties Evaluation

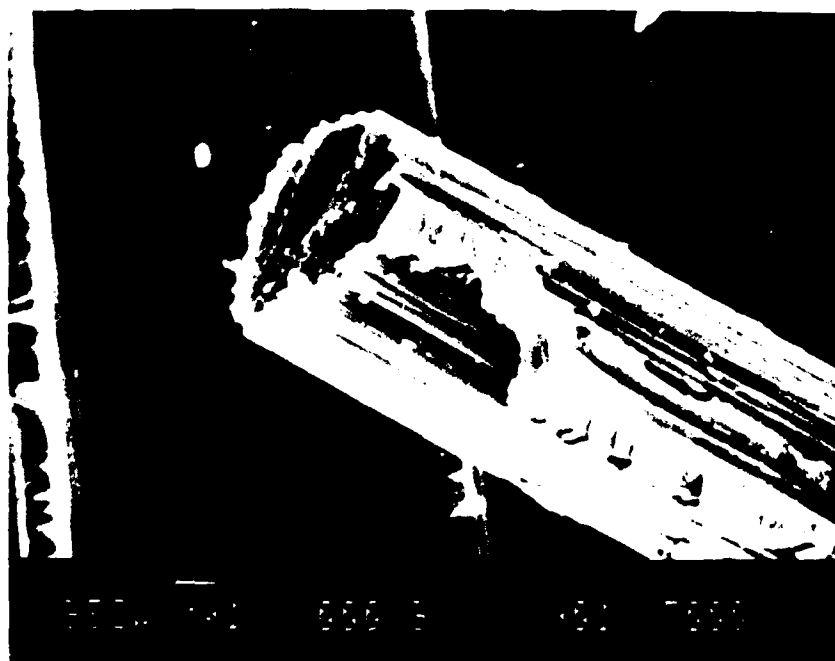
#### 4.4.1 Overview

The initial objective of American Cyanamid in improving the performance of ATB were to: a) exceed RT mechanical properties and toughness of first generation BMIs (like V378A); b) have  $350^\circ\text{F}$  wet service capability; and c) handle and process like conventional epoxies and BMIs. In this section we will review the T-300/CATB-



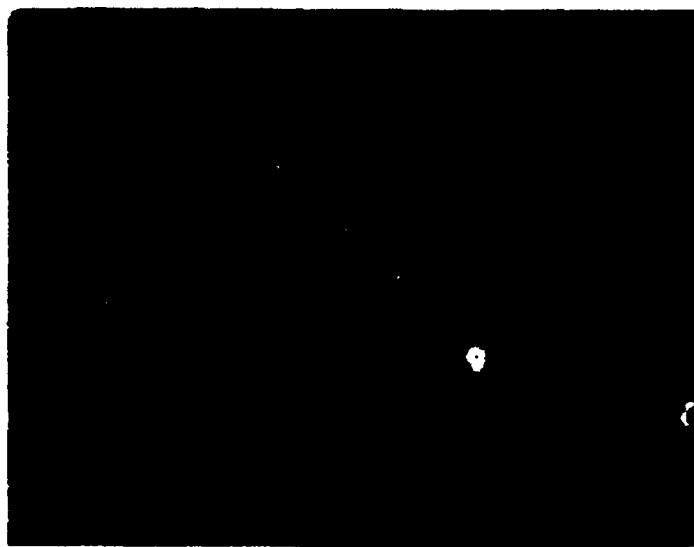


(a)



(b)

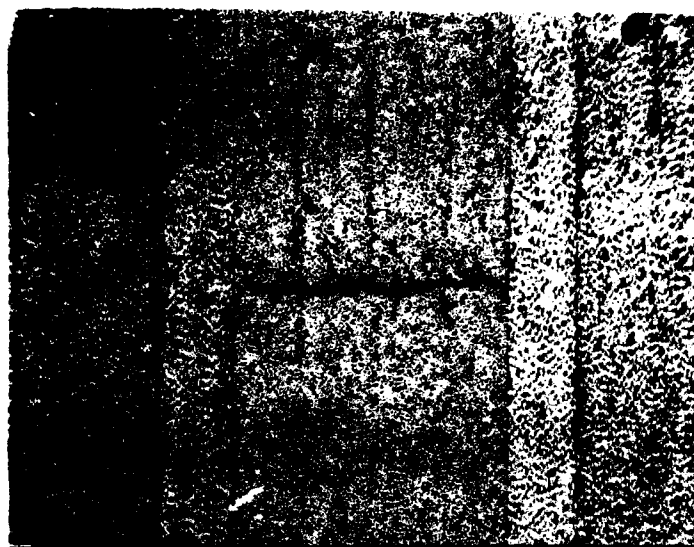
Figure 15. SEM photographs of T-300/CATB-44 Double Cantilever Beam fracture surface.



(a)



(b)



(c)

Figure 16. Photomicrographs of T-300/CATB-44 composite cross sections. "a" is  $[0]_{12}$ ; "b" is  $[\pm 45]_{2S}$ ; and "c" is  $[\pm 30, \pm 30, 90_2]_S$  layup respectively.

44 composite properties measured in this investigation and compare them to those of T-300/V378A composites.

#### 4.4.2 Mechanical Evaluation Results for T-300/CATB-44

Table 5 gives the results of the AFWAL/MLBC mechanical properties evaluation described in Section 3.

##### 4.4.2.1 3-Point Flexure

The RT dry and wet moduli of the T-300/CATB-44 are comparable to those of T-300/V378A, but the strengths are lower. This is not unexpected since the CATB-44 is such a brittle matrix. The 350 dry and wet strength of the T-300/CATB-44 is considerably higher than that of V378A, but the moduli are lower. This is consistent with the behavior of an inverted two-phase matrix. The ductile phase is more compliant and also apparently more moisture absorbent. The water pick-up of pure ATB is reported (Dynes, 1985) to be approximately 0.2%, but the composites in this study absorbed about 1.0%. The unidirectional laminates do not micro-crack or show any significant porosity so the increase in moisture absorption must be due to the toughening phase.

##### 4.4.2.2 4-Point Flexure

The RTd, RTw, 350d, and 350w strengths all show the same trends as did the 3-Point tests. The RT strengths are lower than V378A but the elevated temperature properties are better. There is an anomaly in the behavior of the 350d and 350w moduli of T-300/CATB-44 composite. The moduli are much higher than the V378A for the same conditions. Without further testing of both the CATB-44 and the V378A composites, this issue cannot be resolved.

The 90° flex test is a measure of the matrix and interfacial properties. Under RTd conditions, CATB-44 and V378A composites are comparable in modulus, but the T-300/CATB-44 strength is 20%

Table 5. Mechanical Test Results.

TEST ID	CONDITIONS	V <sub>f</sub> a	%Moisture	T-300/CATB-44	T-300/V378A
				( $\sigma$ KSI, E MSI)	( $\sigma$ KSI, E MSI)
3-pt Flexure	RT dry	0.61	0.0	233.5 KSI/14.5 MSI	270 KSI/14.8 MSI
	RT wet	"	0.88	239.8/ 19.7	254/ 17.7
	350°F dry	"	0.0	202.9/15.2	188/17.6
	350°F wet	"	0.88	165.6/ 7.6	145/ 16.4
4-pt Flexure	RT dry	0.61	0.0	246.8 KSI/ 17.5 MSI	271 KSI/ 15.6 MSI
	RT wet	"	0.93	222.4/ 16.7	233/ 16.2
	350°F dry	"	0.0	194.6/ 17.1	143/ 14.3
	350°F wet	"	0.93	128/ 16.5	104/ 14.0
90° 4-pt Flexure	RT dry	0.61	0.0	8.7 KSI/ 1.5 MSI	10.9 KSI/ 1.5 MSI
	RT wet	"	0.91	6.9/ 1.46	N/A <sup>b</sup>
				( $\tau$ KSI )	( $\tau$ KSI )
Short Beam Shear (SBS)	RT dry	0.61	0.0	13.9 KSI	15.4 KSI
	RT wet	"	1.05	13.3	14.3
	350°F dry	"	0.0	10.7	8.3
	350°F wet	"	1.05	7.3	6.7
4-pt Shear	RT dry	0.61	0.0	12.4 KSI	12.3 KSI
	RT wet	"	1.03	11.7	11.3
	350°F dry	0.65	0.0	8.8	7.2
	350°F wet	"	1.03	5.3	4.5
				( $\sigma$ KSI/ E MSI)	( $\sigma$ KSI/ E MSI)
0° Tension	RT dry	0.61	- -	240.6 KSI/ 17.3 MSI	227 KSI/ 21.6 MSI

Table 5. (continued)

TEST ID	CONDITIONS	V <sub>f</sub> <sup>a</sup>	%Moisture	T-300/CAIB-44	T-300/V378A
In-Plane-Shear (IPS)	RT dry	0.64	0.0	( $\tau$ KSI/ G12 MSI)	( $\tau$ KSI/ G12 MSI)
	350°F dry	"	0.0	10.1/ .95	N/A / .96
	350°F wet	"	1.48	10.9/ .93 6.83 / .58	N/A N/A / .60
Edge Delamination (ED)	RT dry	--	--	(CRACK $\sigma$ KSI)	(CRACK $\sigma$ KSI)
				19.4 KSI	21.3 KSI
Double Cantilever Beam, Mode I	RT dry	--	--	(G <sub>Ic</sub> , in-lb/in <sup>2</sup> )	(G <sub>Ic</sub> , in-lb/in <sup>2</sup> )
				0.677 <sup>c</sup> , 0.632 <sup>d</sup> , 0.594 <sup>e</sup>	0.67
				(G <sub>IIc</sub> , in-lb/in <sup>2</sup> )	(G <sub>IIc</sub> , in-lb/in <sup>2</sup> )
End Notched Flexure, Mode II	RT dry	--	--	1.77 <sup>c</sup> , 1.64 <sup>e</sup>	N/A

<sup>a</sup>this was determined directly by an acid digestion<sup>b</sup>N/A indicates the data was not available<sup>c</sup>indicates the "Area Method" used for calculation<sup>d</sup>indicates the "Beam Theory" used for calculation<sup>e</sup>indicates the "Empirical Method" used for calculation

less than that of T-300/V378A. Further, the RTw strength of the CATB-44 composite drops 21% from the RT d state.

#### 4.4.2.3 Short Beam Shear (SBS) and 4-Point Shear

The SBS and 4-Point shear results are consistent with the trends shown in the flex tests. The RT properties of T-300/CATB-44 are slightly less than T-300/V378A and the elevated temperature properties are slightly higher than T-300/V378A. In order to better understand the interlaminar shear strength (ILSS) of the T-300/CATB-44 composite, it is often enlightening to consider test artifacts in the analysis. The SBS failures were complex with most exhibiting compressive failures. The 4-Point shear specimens, however, all failed in shear along the mid-plane with no visible compressive failures. Thus, if we compare the 4-Point shear strength as a truer measure of ILSS the T-300/CATB-44 is higher than the T-300/V378A for all test conditions.

#### 4.4.2.4 0° Tension

The 0° tensile strengths of the T-300/CATB-44 is 6% higher than for the T-300/V378A. The modulus of T-300/V378A, however, is 25% higher. The strain to failure of the T-300/CATB-44 is almost 40% higher than for the T-300/V378A. This is most likely due to the toughening phases' ability to retard crack growth through ductile deformation mechanisms.

#### 4.4.2.5 In-Plane Shear (IPS)

Only RTd and 350w IPS modulus data are available for T-300/V378A so our basis for comparison is rather limited. The two composite materials appear to be roughly equivalent over the spectrum with no difference outside of experimental error.

#### **4.4.2.6 Other Mechanical Tests: Edge Delamination; Mode I; and Mode II**

The properties of T-300/CATB-44 and T-300/V378A are approximately equivalent. Their interlaminar fracture toughness measured by these three methods is comparable to other brittle epoxies and BMIs.

#### **4.4.3 General Discussion of the Mechanical Behavior of T-300/CATB-44**

Dynes (1985) reported 70% to 80% retention of ILSS and flexural properties at 350°F for pure AS-4/ATB composites and stated that the properties were insensitive to moisture. The T-300/CATB-44, however, exhibits typically 50% to 70% retention of those same properties. This supports the thermal analysis data and moisture absorption evidence that the toughening phase has poor "hot/wet" capability. It is not a good strategy to use a toughening phase with those inherent weaknesses as the continuous phase of a structural composite matrix. Since the inverted two-phase morphology is not distinct in the composite it is probable that the neat resin would have even poorer retention of hot/wet properties than did the T-300/CATB-44 composite.

## SECTION 5. CONCLUSIONS AND RECOMMENDATIONS

T-300/CATB-44 offers no advantage over first first generation bismaleimide composites as an aerospace structural material for 350°service. The interfacial bonding needs to be improved as does the method used to toughen the brittle ATB base resin. The results of this investigation indicate that the continuous toughening phase is responsible for the moisture problems of CATB-44. The following recommendations are suggested to improve the service capability of ATB formulated resins:

- a. Do not use inverted two-phase morphology for toughening. Develop system with spinodal composition or continuous brittle phase with discrete toughening domains.
- b. Improve interface. Dynes (1985) showed that the pure ATB did not have a good interface and this study showed poor adhesion for the formulated system.

Additionally, handling characteristics need to be improved if the ATB formulations are to be used in more than test coupon-type evaluations.



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